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(54) **Manufacture of powder cores for electromagnetic apparatus.**

(57) Ferromagnetic glassy metal powder is compacted with static pressure of 69 to 690 MPa at a temperature in the vicinity of the glass transition temperature and below the crystallization temperature thereof to form a consolidated, magnetic glassy metal alloy body. The resulting compacts can be annealed to enhance ferromagnetic properties. Consolidated bodies exhibit low core loss and permeabilities which remain constant over a wide frequency range.

EP 0 092 091 A2

DESCRIPTION

MANUFACTURE OF POWDER CORES FOR ELECTROMAGNETIC APPARATUS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to magnetic articles made as cores and pole pieces and to a process for making them from metallic glass powder.

Description of the Prior Art

Amorphous metal alloys and articles made therefrom are disclosed by Chen and Polk in United States Patent 3,856,513 issued December 24, 1974. That patent teaches certain novel metal alloy compositions which are obtained in the amorphous state and are superior to previously known crystalline alloys based on the same metals. The compositions taught therein are easily quenched to the amorphous state and possess desirable physical properties. The patent discloses further that amorphous metal powders having a particle size ranging from 10 to 250 μm can be made by grinding or air milling the cast ribbon.

Manufacture of magnetic articles by consolidation of permalloy and other crystalline alloy powders is known. New applications requiring improved magnetic properties have necessitated efforts to develop alloys and consolidation processes that increase, concomitantly, the strength and magnetic response of magnetic articles.

SUMMARY OF THE INVENTION

The present invention provides amorphous metal

alloy powders especially suited for consolidation into bodies having excellent magnetic response. In addition, the invention provides a method for manufacture of magnetic articles in which consolidation of glassy metal powder is effected using a thermomechanical process and insulating materials.

Articles produced in accordance with the method of this invention have low remanence and permeabilities which remain constant over a wide frequency range. Typically, such consolidated magnetic glassy metal alloy bodies have a relative magnetic permeability of at least 15. As used herein, the term "relative permeability" is intended to mean the ratio of the magnetic induction in a medium generated by a certain field to the magnetic induction in vacuum generated by the same field.

More specifically, molded magnetic metal alloy articles are produced in accordance with the invention by a method comprising the step of compacting ferromagnetic glass powder with static pressure at a pressing temperature in the vicinity of the glass transition temperature and below the crystallization temperature of said alloy, and at a pressure of 69 MPa to 690 MPa. A consolidated, glassy metal alloy body is thereby formed, which is especially adapted to be post fabrication annealed at a temperature ranging from 380 to 450°C for a time period of 1 to 4 hours in the presence of a magnetic field of 0 to 800 A/m. The annealed article has improved impedance permeability and is particularly suited for use in signal and high frequency power transformers and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the preferred embodiments of the invention and the accompanying drawings, in which:

Fig. 1 is a schematic representation of

apparatus used to cast amorphous metal powder directly from the melt, the apparatus having a serrated casting substrate;

Fig. 2 is a graph showing variation in density of consolidated objects as a function of pressing time and temperature;

Fig. 3 is a graph showing variation in impedance permeability as a function of post fabrication anneal time;

Fig. 4 is a graph showing variation in impedance permeability as a function of frequency of uninsulated and insulated powders;

Fig. 5 is a graph showing variation in impedance permeability as a function of frequency of cores made of different particle sizes; and

Fig. 6 is a graph showing the variation in core loss as a function of post fabrication anneal time.

DETAILED DESCRIPTION OF THE INVENTION

The magnetic compact bodies with permeability greater than 15 of the present invention are generally made from glassy metal alloys in powder form. The general process for preparing metallic glass powders from alloys involves a step of rapid quenching and a step of atomization. Alloys are cast directly into ribbon, followed by grinding, ball milling or air milling into powders or flakes of desirable size range. To aid the pulverization process, ribbon samples are subjected to an embrittlement heat treatment below the crystallization temperature of the alloy.

Alternatively, powders or flakes, defined herein as particles with the major diameter more than an order of magnitude smaller than their thickness, can be cast directly into the final form having a desirable size range using a serrated casting substrate of the type illustrated in Figure 1. The size of the particles or flakes thereby produced will vary, depending on the depth of the serrations and the distance therebetween. Typically the serrations comprise a plurality of

regularly spaced peaks and valleys, the distance between adjacent peaks ranging from 0.01 cm to 0.1 cm and the distance from the top of a peak to the bottom of a valley ranging from 0.005 cm to 0.05 cm. Such configuration of the casting substrate typically yields powder particles or flakes having a size ranging from 0.01 cm to 0.1 cm.

As shown in Figure 1, the apparatus 10 has a movable chill surface 12, a reservoir 14 for holding molten metal 16 and a nozzle 18 in communication at its top with reservoir 14 and having at its bottom an opening 20 in close proximity to the chill surface 12. The chill surface 12 has a plurality of regularly spaced peaks 22 and valleys 24. Adjacent peaks are separated by a distance, d, of 0.01 cm to 0.1 cm. The distance, y (not shown), from the top of a peak to the bottom of a valley is 0.005 cm to 0.05 cm. Powder is produced directly by deposition of molten alloy on the serrated substrate (chill surface 12) which is a rotatable chill roll, an endless belt (not shown) or the like, adapted for longitudinal movement at a velocity of 100 to 200 meters per minute. The size of the powder particles thereby produced varies directly with the magnitude of distances d and y.

In the embodiment shown, the nozzle means has a slot arranged generally perpendicular to the direction of movement of the chill surface. The slot is defined by a pair of parallel lips, a first lip and a second lip numbered in the direction of movement of the chill surface. The slot of nozzle 18 has a width of from 0.2 to 1 millimeter, measured in the direction of movement of the chill surface. The first lip has a width at least equal to the width of the slot, and the second lip has a width of from 1.5 to 3 times the width of the slot. The gap between the lips and the chill surface is from 0.1 to 1 times the width of the slot. The preparation of a glassy alloy can be achieved by following the basic teaching

set forth in U.S.P. 3,856,553 to Chen, et al. The resulting sheets, ribbons, tapes and wires are useful precursors of the materials disclosed here.

Consolidation of the powder is the initial step in producing a body. Powder adapted for consolidation can comprise fine powder (having particle size under 105 micrometers), coarse powder (having particle size between 105 micrometers and 300 micrometers) and flake (having particle size greater than 300 micrometers). Consolidation can be obtained by pressing glassy metal alloy powder near its glass transition and below the crystallization temperature.

In case low permeabilities (i.e., less than 25) are desired, a particle diameter of less than 105 micrometers is used. For high permeabilities (greater than 100), larger particle diameters of 300 micrometers or more are employed.

For consolidation, powders can be put in evacuated cans and then be formed to strips or isostatically pressed to discs, rings or any other desirable shape such as transformer and inductor cores, motor stators and rotor parts, and the like. Furthermore, powders can be warm pressed below the crystallization temperature and in the region of glass transition temperature into any desirable shapes of transformer/inductor cores or motor rotor/stator segments. Consolidation is believed to result from mechanical interlocking and short-range diffusion bonding between the powder or flake particles occurring in the vicinity of the glass transition temperature. At temperatures too far below the glass transition temperature (Tg) the particles are relatively hard and are not readily deformed by shear and compressive forces exerted thereon during consolidation. Temperatures too far above Tg enhance the risk of incipient crystallization of the amorphous particles during consolidation. Generally, it has been found that interpartical bonding is best

achieved during consolidation at pressing temperatures within 50°C of Tg.

The powders can also be mixed with a suitable organic binder, for instance, paraffin, polysulfone, polyimide, phenolic formaldehyde resins, and then cold pressed to suitable forms. The amount of binder can be up to 30 weight percent and is preferably less than 10 weight percent and more preferably between 0.5 and 3 weight percent for high permeability cores. Such formed alloy can have a density of at least 60 percent of the theoretical maximum. The pressed object can be cured at a relatively low temperature below the curing temperature of the binder to give more strength and then ground to final dimensions. The preferred product of this process comprises shapes suitable as magnetic components. The curing process can be performed with simultaneous application of a magnetic field.

A metallic glass is an alloy product of fusion which has been cooled to a rigid condition without crystallization. Such metallic glasses generally have at least some of the following properties: high hardness and resistance to scratching, great smoothness of a glassy surface, dimensional and shape stability, mechanical stiffness, strength, ductility, high electrical resistance compared with related metals and alloys thereof, and a diffuse X-ray diffraction pattern.

The term "alloy" is used herein in the conventional sense as denoting a solid mixture of two or more metals (Condensed Chemical Dictionary, Ninth Edition, Van Norstrand Reinhold Co., New York, 1977). These alloys additionally contain admixed at least one non-metallic element. The terms "glassy metal alloy," "metallic glass," "amorphous metal alloy" and "vitreous metal alloy" are all considered equivalent as employed herein.

Alloys suitable for the processes disclosed in the present invention include the composition

$[Fe,Ni,Co]_{65-88}[Mo,Nb,Ta,Cr,V]_{0-10}[B,C,S]_{5-25}$.

Preferred ferromagnetic alloys according to the present invention are based on one member of the group consisting of iron, cobalt and nickel. The iron based alloys have the general composition $Fe_{40-88}(Co,Ni)_{0-40}(Mo,Nb,Ta,V,Cr)_{0-10}(B,C,Si)_{5-25}$; the cobalt based alloys have the general composition $Co_{40-88}(Fe,Ni)_{0-40}(Mo,Nb,Ta,V,Mn,Cr)_{0-10}(B,C,Si)_{5-25}$ and the nickel based alloys have the general composition $Ni_{40-84}(Co,Fe)_{4-40}(Mo,Nb,Ta,V,Mn,Cr)_{0-10}(B,C,Si)_{5-25}$.

An especially preferred alloy has the composition 79 atomic percent iron, 16 atomic percent boron and 5 atomic percent silicon.

Amorphous metallic powders can be compacted to fabricate parts suitable for a variety of applications such as electromagnetic cores, pole pieces and the like. The glassy metal compacts have either high or low permeability. The resulting cores can be used as transformer cores, motor stators or rotors and in other alternating current applications. Amorphous alloys that are preferred for such applications include $Fe_{78}B_{13}Si_4$, $Fe_{79}B_{16}Si_5$ and $Fe_{81}B_{13.5}Si_{3.5}C_2$.

The following examples are presented to provide a more complete understanding of the invention. The specific techinques, conditions, materials, proportions and reported data set forth to illustrate the principles and practice of the invention are exemplary and should not be construed as limiting the scope of the invention.

Example 1

Amorphous metallic powders having a particle size below 300 μm and a composition of $Fe_{79}B_{16}Si_5$ (subscripts in atom percent) were prepared by air milling ribbon cast directly from the melt according to the procedure detailed in U.S. patent 4,142,571. Cast ribbon was also given an embrittlement treatement in an inert nitrogen atmosphere for 1-2 hours at 400°C prior to ball milling for 16 hours. The above processes

resulted in fine amorphous particles ranging from 300-10 μm. The resulting fine powder particles were sieved into different size ranges, namely "-325 mesh" ($\leq$ 40 μm), "-150 mesh" ($\leq$ 105 μm) and "-48 mesh" ($\leq$ 300 μm). Powders were then coated with either 1-3 wt% SiO_2 by mixing the particles with a slurry containing SiO_2 and methanol or 1 wt% MgO using a slurry containing M_gO and methanol. The coated powders of -150 and -325 mesh size were then pressed in graphite molds at temperatures, ranging from 410-510°C for 5, 15 and 30 minutes. The pressure employed was 69 MPa. Since the glass transition temperature (Tg) cannot be accurately determined for the $Fe_{79}B_{13}Si_9$ alloy, warm pressing was conducted over a wide temperature range 410-510°C below the crystallization temperature Tx(=530°C). Variation of core density as a function of pressing conditions is shown in Figure 2. Approximately 80-85% of ideal density can be achieved at 460°C, 1/2 hr. However, pressing time can be shortened at higher temperatures to achieve the same density. Also, various molds can be fabricated to warm press directly into the desired shape, namely rods, toroid, EI shapes etc. necessary for the specific applications.

Example 2

Amorphous metallic powder particles with size below 105 μm of an alloy and a composition of $Fe_{79}B_{16}Si_5$ were prepared by air milling as indicated in Example 1 and also by ball milling after embrittling the as-cast ribbon by heat treating at 400°C for 1 hr. Air milled powder particles were coated with 1 wt% MgO. Toroidal cores (ID = 25 mm, OD = 38 mm & thickness = 12 mm) were fabricated by warm pressing at 430°C for 1/2 hr. To evaluate the effect of a post fabrication anneal, pressed cores made from both insulated and uninsulated powders were annealed at 435°C for 1 to 4 hrs. and the corresponding impedance permeability values were determined and plotted in Figure 3.

A post fabrication anneal substantially

improves the permeability and the optimum anneal was found to be 1-2 hrs. at 435°C for the specific composition and consolidation process employed in the present example.

Example 3

Amorphous metallic powder particles with size below 105/μm of an alloy and a composition of $Fe_{79}B_{16}Si_5$ were prepared by air milling as indicated in Example 1.

To evaluate the effects of insulation, toroidal cores (I.D. = 25 mm, O.D. = 38 mm and thickness = 12 mm) were prepared with 1-3 wt% SiO_2 or MgO by warm pressing at 430°C for 1/2 hr. Fabricated cores were then annealed at 435°C for 1 hr. and their impedance permeability was determined as a function of frequency (1-100 kHz at .1 Tesla induction). The results are illustrated in Figure 4. The impedance permeability for the insulated powder cores does not change with frequency; whereas, the permeability for the uninsulated cores rolls off with frequency due to eddy current shielding. This constant permeability is a very important magnetic characteristic desirable for signal and high frequency power transformer applications.

Example 4

Amorphous metallic powder particles having two different size ranges, namely "-48 mesh size" (≤ 300 μm) and "-150 mesh size" (≤105 μm) were prepared by air milling in accordance with the procedure set forth in Example 1. Powder particles were coated with 1 wt % MgO pressed to toroidal samples (ID = 25 mm, OD = 38 mm and thickness = 12 mm) and post fabrication annealed at 435°C for 1-2 hrs. Impedance permeability values of the cores were plotted as a function of frequency. As shown in Figure 5, higher permeability was obtained with coarser particle size.

Example 5

Core loss characteristics, in addition to impedance permeabilities, are important to power transformer core applications. Toroidal cores (ID = 25 mm, OD = 38 mm, thickness = 12 mm) were

prepared from insulated (1% MgO) powder of particle size -48 and -150 mesh using the same alloy $Fe_{79}B_{16}Si_5$ and the same fabricaton technique described in Example 1. Fabricated cores were annealed at 435 for 1-3 hrs. Core loss values at 50 kHz/.1 Tesla are shown in Figure 5. Optimum heat treatment appears to be greater than 2 hrs. at 435°C. High frequency core loss values are substantially reduced with a smaller particle size and 1-3% by weight insulation. Powder and insulation characteristics necessary for optimum low frequency (60-400 Hz) core loss are substantially different fom those necessary for high frequency applications. Since eddy currents are not dominant at lower frequencies, larger particle size (eg. greater than 300 μm) with no insulation is desirable for 60-400 Hz transformer and motor applications. Also, for such lower frequency transformer and motor applications, post fabrication annealing should be conducted at lower temperatures, as in the order of temperatures ranging from 380 to 420°C, to avoid partial crystallization, of the amorphous matrix. For high frequency applications, the particle size is smaller (eg. less than 105 micrometers), the particles are coated with an insulator such as MgO, SiO_2 or the like, and the annealing temperature ranges from 420-450°C.

Having thus described the invention in rather full detail it will be understood that these details need not be strictly adhered to but that various changes and modifications may suggest themselves to one skilled in the art, all falling within the scope of the invention as defined by the subjoined claims.

Claims:

1. A method for making molded magnetic metal alloy articles, comprising the step of

compacting ferromagnetic glass powder with static pressure at a pressing temperature in the vicinity of the glass transition temperature and below the crystallization temperature of said alloy and at a pressure of 69 MPa to 690 MPa to form a consolidated, magnetic glassy metal alloy body.

2. A method as recited in claim 1, wherein said compacting step is carried out for a time period of 1 to 60 minutes.

3. A method as recited in claim 2, wherein said powder is composed of particles having a particle diameter of less than 105 micrometers.

4. A method as recited in claim 1, wherein said powder is composed of particles having a particle diameter of at least 300 micrometers.

5. A method as recited in claim 3, including the step of coating said particles with an insulator prior to said compacting step.

6. A method as recited in claim 5, wherein said particles are pressed in graphite molds during said compacting step at a temperature ranging from 410 to 510°C and for a time period from 5 to 30 minutes.

7. A method as recited in claim 2, including the step of annealing said consolidated alloy body at a temperature of ranging from 380 to 450°C for a time period of 1 to 4 hours.

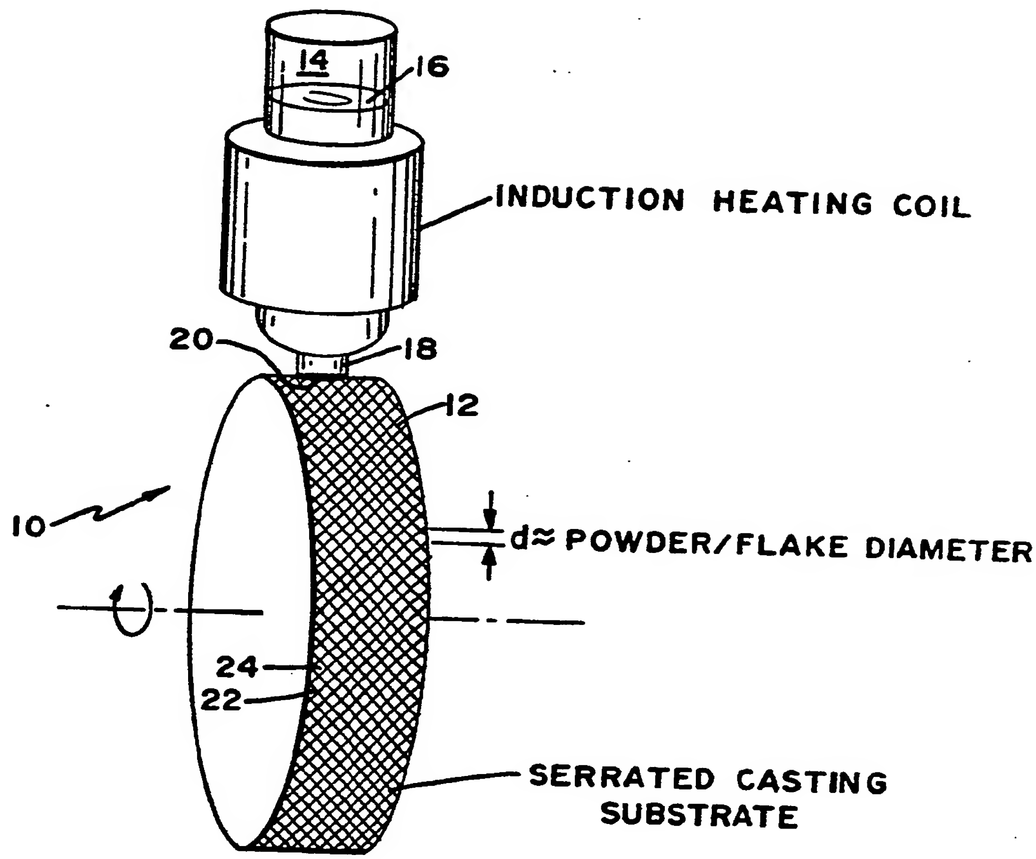
8. A method as recited in claim 7, wherein said annealing step is carried out in the presence of a magnetic field of 0 to 800 A/m.

9. An apparatus for casting of metal powder comprising a movable chill surface, a reservoir for holding molten metal and a nozzle in communication at its top with the reservoir and having at its bottom an opening in close proximity to the chill surface, wherein

a. the chill surface has a plurality of regularly spaced peaks and valleys, the distance between adjacent peaks ranging from 0.01 cm to 0.1 cm and the distance from the top of a peak to the bottom of a valley ranges from 0.005 cm to 0.05 cm; and

b. the chill surface is adapted for longitudinal movement at a velocity of 100 to 2000 meters per minute.

10. Apparatus as recited in claim 9, wherein said nozzle means has a slot arranged generally perpendicular to the direction of movement of said chill surface, the slot being defined by a pair of generally parallel lips, a first lip and a second lip numbered in the direction of movement of the chill surface, wherein said slot has a width of from 0.2 to 1 millimeter, measured in direction of movement of the chill surface, wherein the first lip has a width at least equal to the width of said slot, and said second lip has a width of from 1.5 to 3 times the width of said slot, and wherein the gap between the lips and the chill surface is from 0.1 to 1 times the width of the slot.



14
16
INDUCTION HEATING COIL
20
18
12
10
d≈ POWDER/FLAKE DIAMETER
24
22
SERRATED CASTING SUBSTRATE

FIG. 1

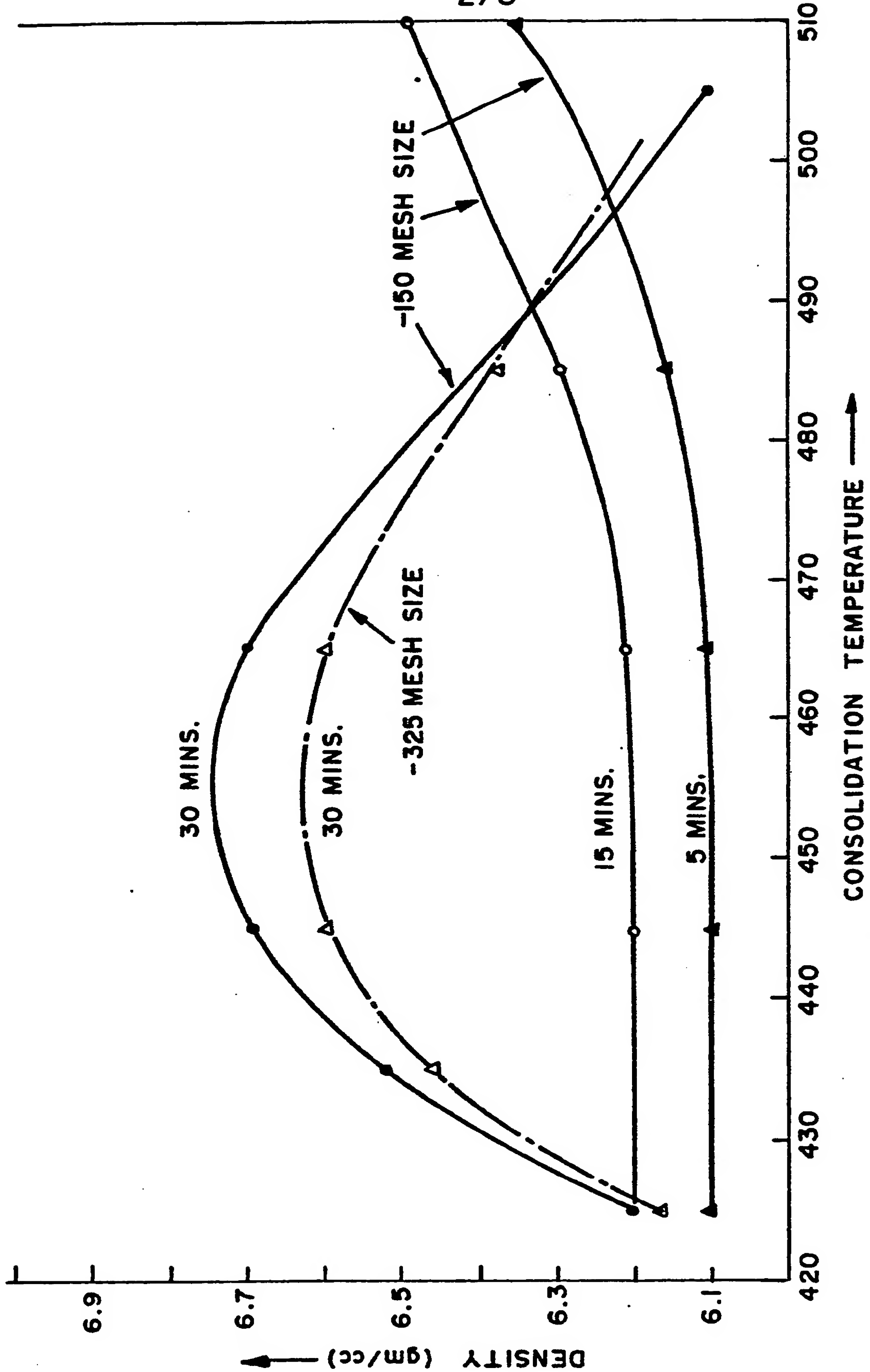

DENSITY (gm/cc)
6.1
6.3
6.5
6.7
6.9
CONSOLIDATION TEMPERATURE
420
430
440
450
460
470
480
490
500
510
30 MINS.
30 MINS.
-325 MESH SIZE
15 MINS.
5 MINS.
-150 MESH SIZE

FIG. 2

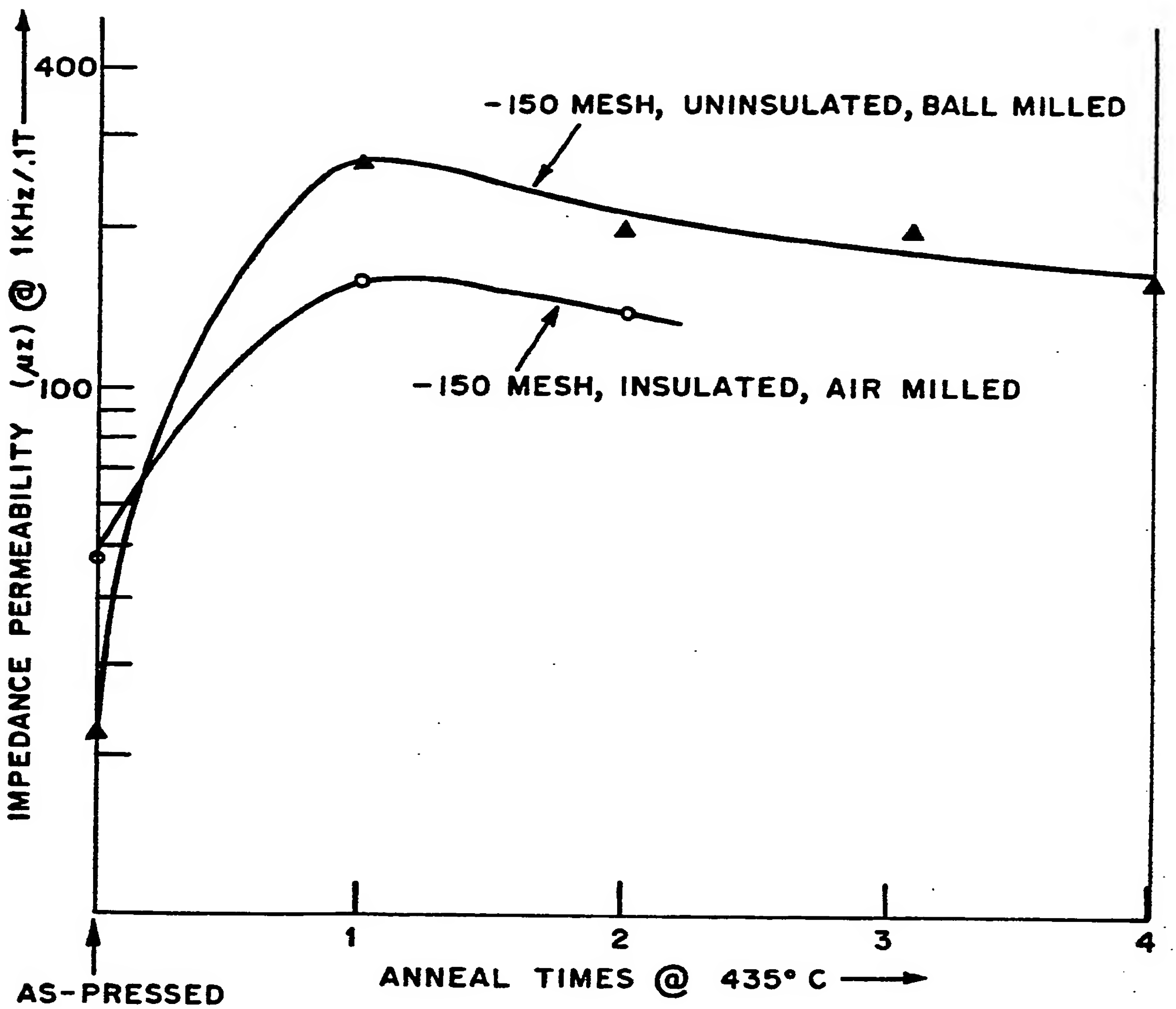

400
100
IMPEDANCE PERMEABILITY (μz) @ 1KHz/.1T
-150 MESH, UNINSULATED, BALL MILLED
-150 MESH, INSULATED, AIR MILLED
1
2
3
4
AS-PRESSED
ANNEAL TIMES @ 435° C

FIG. 3

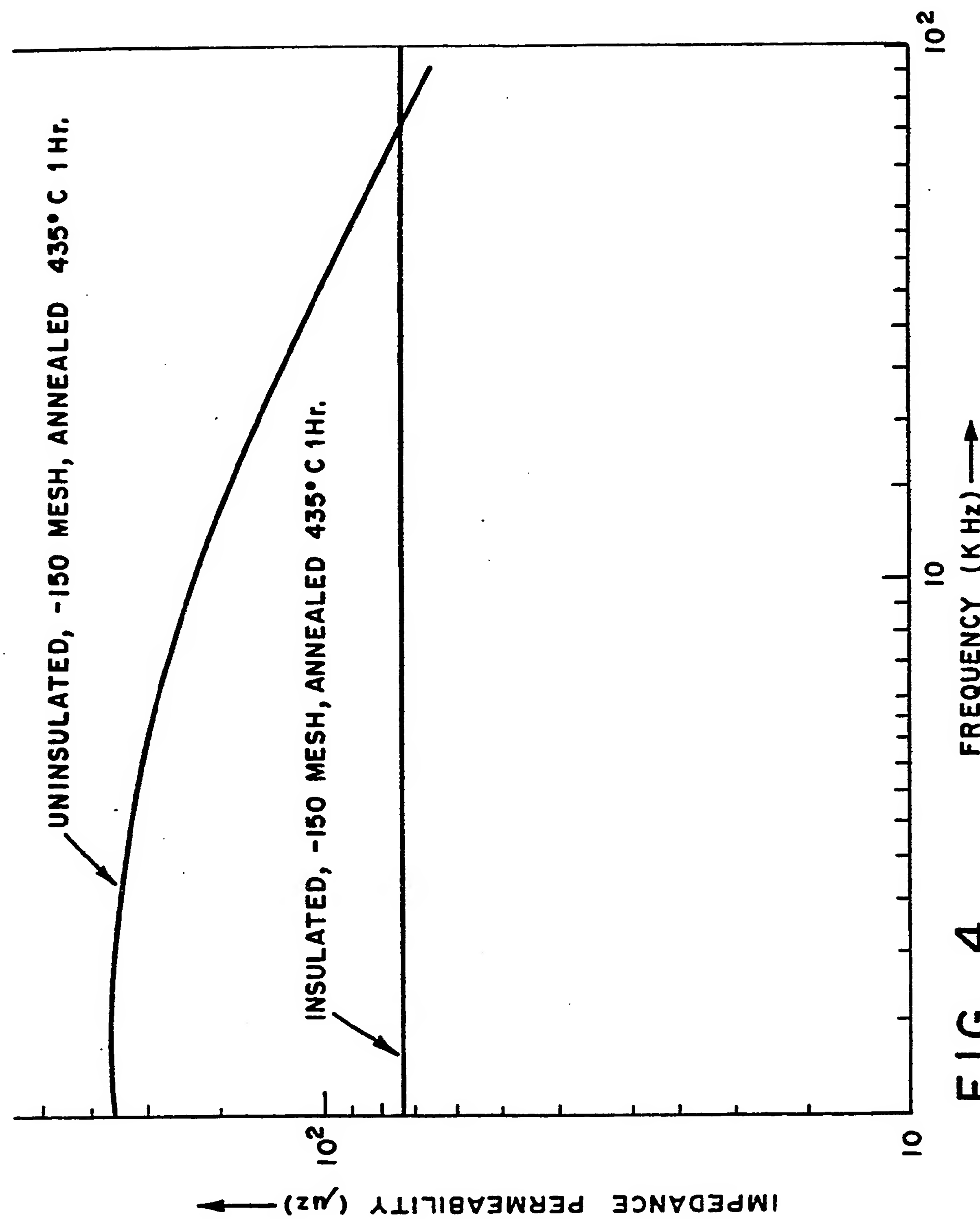

UNINSULATED, -150 MESH, ANNEALED 435° C 1 Hr.
INSULATED, -150 MESH, ANNEALED 435° C 1Hr.
10
10
10^2
10^2
FREQUENCY (K Hz)
IMPEDANCE PERMEABILITY (μz)

FIG. 4

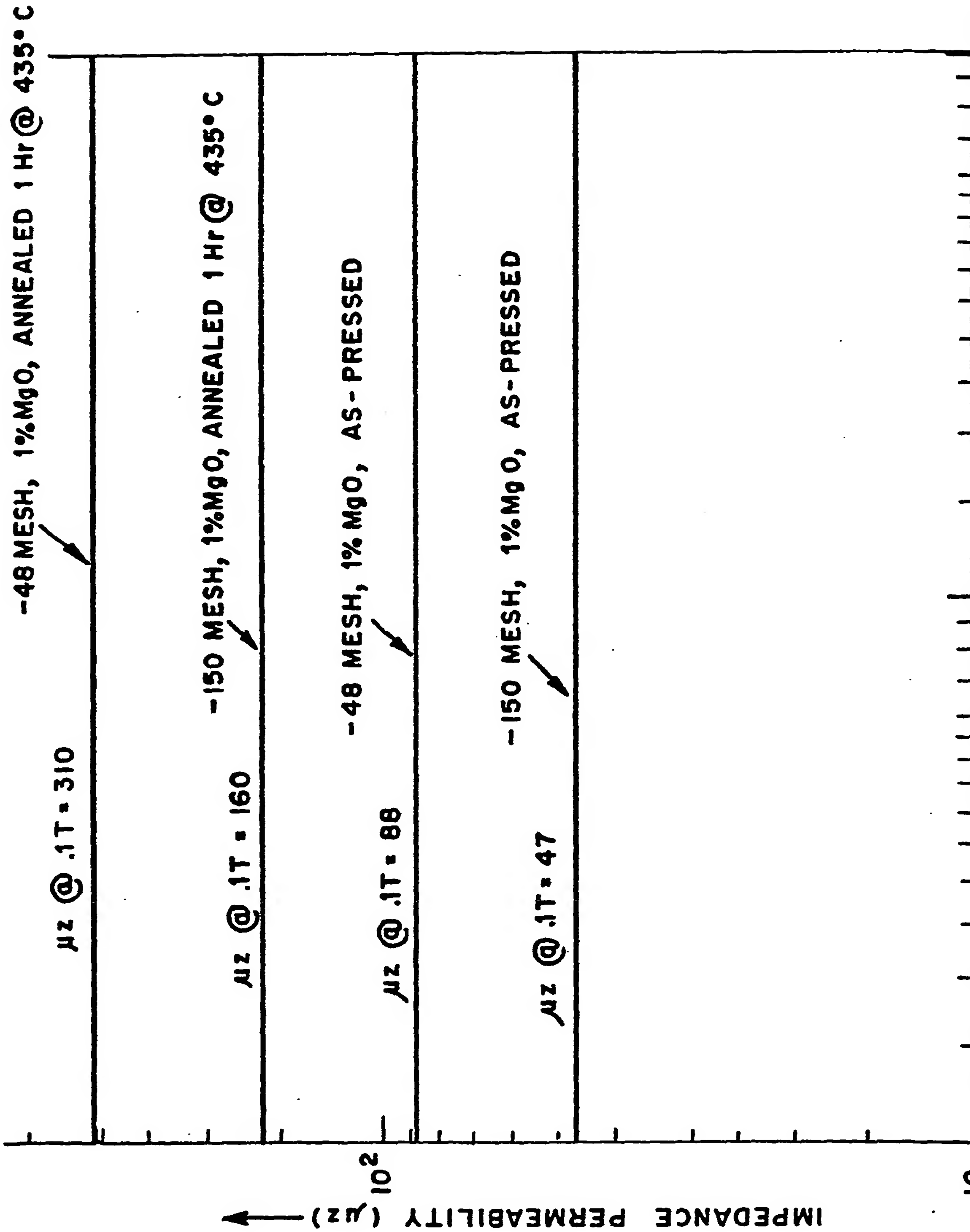

-48 MESH, 1% MgO, ANNEALED 1 Hr @ 435° C
μz @ .1T = 310
-150 MESH, 1% MgO, ANNEALED 1 Hr @ 435° C
μz @ .1T = 160
-48 MESH, 1% MgO, AS-PRESSED
μz @ .1T = 88
-150 MESH, 1% MgO, AS-PRESSED
μz @ .1T = 47
10
10^2
FREQUENCY (KHz)
10
10^2
IMPEDANCE PERMEABILITY (μz)

FIG. 5

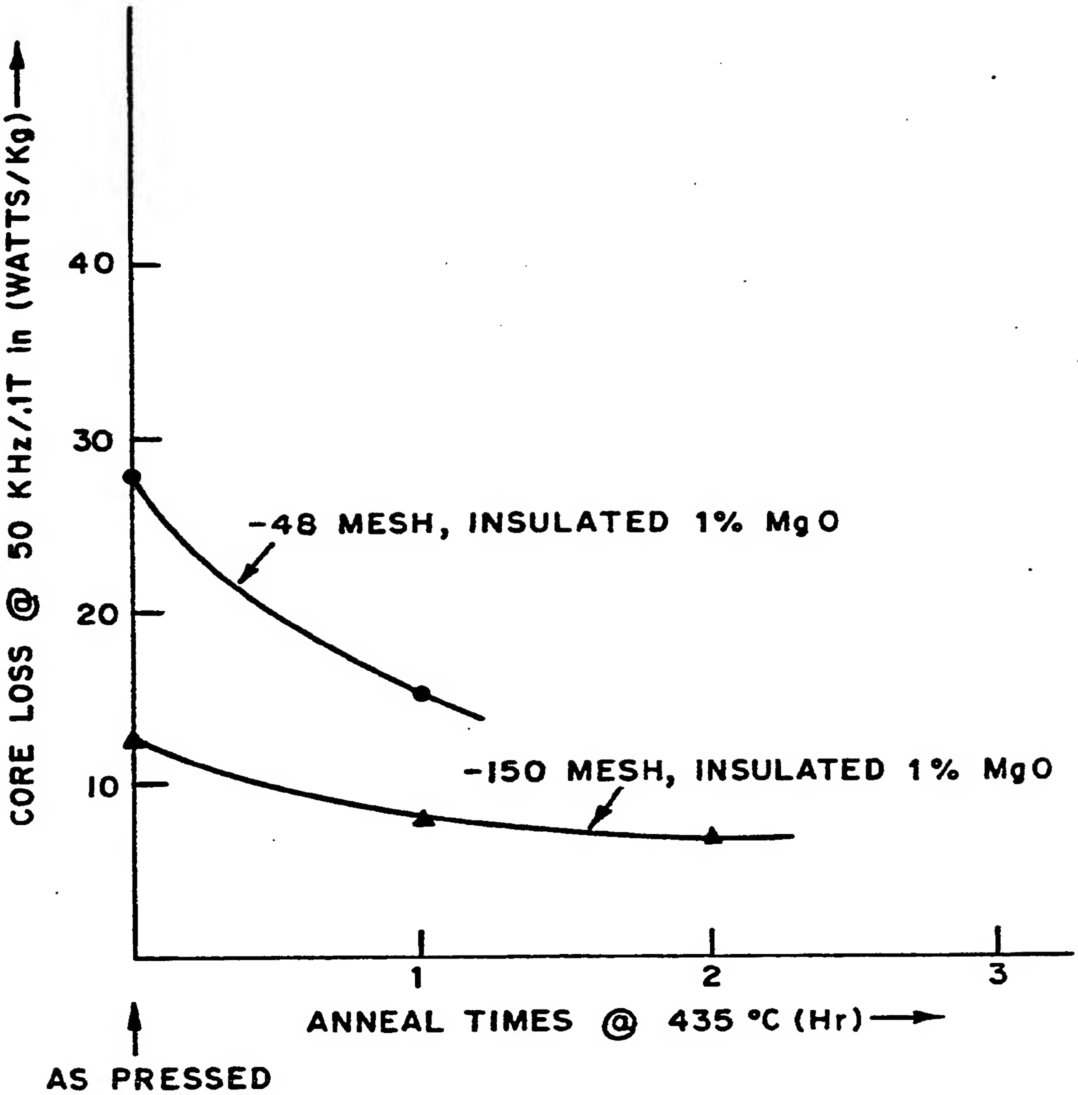

CORE LOSS @ 50 KHz/.1T in (WATTS/Kg)
40
30
20
10
-48 MESH, INSULATED 1% MgO
-150 MESH, INSULATED 1% MgO
1
2
3
ANNEAL TIMES @ 435 °C (Hr)
AS PRESSED

FIG. 6

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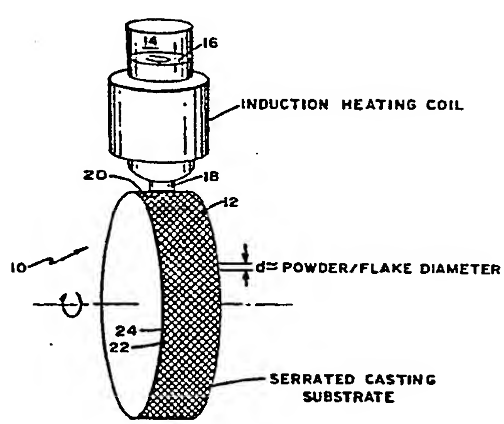

FIG. 1

EP 0 092 091 A3

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 83103269.3

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
A	EP - A1 - 0 035 644 (ALLIED CHEMICAL) * Page 4, line 8 - page 5, line 13; page 6, line 8 - page 8, line 21 *	1-8	H 01 F 1/22 C 22 C 33/00 C 22 C 38/52 H 01 F 1/06
A	DE - A1 - 2 628 207 (DRALORIC) * Claims 7-9; page 6, paragraph 3 - page 7, paragraph 2 *	1,5-7	
A	US - A - 4 116 728 (BECKER) * Column 4, line 43 - column 7, line 20; fig. 1-6 *	1,8	
A	EP - A1 - 0 035 037 (SUMITOMO) * Page 12, paragraph 3 - page 15, paragraph 2; fig. 1-4 *	9,10	TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
A,D	US - A - 4 142 571 (NARASIMHAN) * Column 4, line 61 - column 5, line 52; column 7, line 23 - column 8, line 14; fig. 1-3 *	9,10	B 22 D 11/00 B 22 F 3/00 B 41 C 1/00 C 21 D 1/00 C 22 C 1/00 C 22 C 33/00 C 22 C 38/00 H 01 F 1/00
A,D	US - A - 3 856 513 (CHEN) * Column 2, line 58 - column 6, line 39 *		
A,D	US - A - 3 856 553 (HAYASHI)		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	01-12-1983	PIRKER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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